

UNITED STATES PATENT APPLICATION

OF

**MICHAEL B. KORZENSKI
THOMAS H. BAUM
CHONGYING XU
ELIODOR G. GHENCIU**

FOR

**REMOVAL OF MEMS SACRIFICIAL LAYERS USING SUPERCRITICAL
FLUID/CHEMICAL FORMULATIONS**

EXPRESS MAIL CERTIFICATE OF MAILING

Express Mail Label Number: EV132466644US
Date of Deposit: December 1, 2003

REMOVAL OF MEMS SACRIFICIAL LAYERS USING SUPERCRITICAL FLUID/CHEMICAL FORMULATIONS

FIELD OF THE INVENTION

[0001] The present invention relates to supercritical fluid-based compositions useful in semiconductor manufacturing for the removal of sacrificial layers, e.g., silicon or silicon oxide, from Micro Electro Mechanical System (MEMS) substrates having such sacrificial layers. The compositions also have utility for removing post-ash and post-etch residue.

DESCRIPTION OF THE RELATED ART

[0002] Micro Electro Mechanical Systems (MEMS) are devices that integrate mechanical and electrical components on a single silicon wafer. The electrical and mechanical components are fabricated using traditional integrated circuit (IC) techniques and “micromachining” processes, respectively. Micromachining is used to produce a number of mechanical devices on the wafer that are able to sense and control the environment, including cantilever beams, hinges, accelerometers, microsensors, microactuators and micromirrors.

[0003] The mechanical components on a MEMS wafer are created by depositing sacrificial and structural layers onto a substrate followed by selective etching of the sacrificial layer relative to the structural layer, leaving behind a suspended or freestanding micromechanical structure, such as a beam or a lever. A major problem with fabricating MEMS structures is that as aqueous based etching of the sacrificial layer proceeds, stiction may occur, wherein the surface adhesion forces are higher than the mechanical restoring force of the microstructure. In effect, the microstructure bends down toward the substrate and sticks to it, generally permanently. Proposed causes of stiction include; van der Waals forces, hydrogen bridging and/or electrostatic attractions between the microstructure and the substrate, surface tension forces generated from diminishing liquid menisci trapped in the etched space, and etch by-products precipitating out of solution during drying steps.

[0004] Several methods of minimizing stiction have been proposed, including wet etching with HF, increasing surface roughness to minimize the surface tension energy, and eliminating water by drying the structures with a liquid that has no or little surface tension, e.g., isopropanol (IPA). Proposed alternative water-free etching compositions include anhydrous HF gas, which does not leave residues. However, etching with neat anhydrous HF can require up to ten hours to form complex microstructures and as such, the presence of some water is necessary to initiate the etch reaction thereby eliminating the advantages of using a water-free etchant.

[0005] Alternatively, supercritical fluids (SCF) can be used to etch MEMS devices. Because of low viscosity and near zero surface tension, SCFs avoid many of the problems associated with typical wet processes. For example, because SCFs exhibit a gas-like density, surface tension forces are low and thus the microstructure does not stick to the substrate. Because of high diffusion rates, SCFs can generally penetrate a solid sample faster than liquid solvents. Further, SCFs can rapidly transport dissolved solutes because of their low viscosity. However, SCFs are highly non-polar and as such, many contaminant species are not adequately solubilized therein.

[0006] There is therefore a continuing need in the field for improved etching compositions, since the etching of sacrificial layers from semiconductor substrates is critical to ensure proper production and operation of MEMS devices and emerging integrated circuits.

SUMMARY OF THE INVENTION

[0007] The present invention relates to supercritical fluid-based compositions useful in semiconductor manufacturing for the etching of sacrificial silicon-containing layers from semiconductor substrates, and methods of using such compositions for removal of same.

[0008] Further, the present invention relates to supercritical fluid-based compositions useful in semiconductor manufacturing for the removal of post-ash and post-etch residue from semiconductor surfaces, and methods of using such compositions for removal of same.

[0009] In one aspect, the invention relates to a sacrificial silicon-containing layer etching composition, comprising a supercritical fluid, at least one co-solvent, at least one etchant species, and optionally at least one surfactant.

[0010] In another aspect, the invention relates to a method of removing silicon-containing substances from a substrate having same thereon, said method comprising contacting the substrate with a SCF-based composition comprising a SCF, at least one co-solvent, at least one etchant species, and optionally at least one surfactant, for sufficient time and under sufficient contacting conditions to remove the silicon-containing substances from the substrate.

[0011] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is a control sample before SCF-based etching composition processing including a silicon substrate, a 100 nm thick silicon oxide film on the substrate and a 100 nm thick polysilicon film on the oxide.

[0013] Figure 2 is the control sample in Figure 1 after the sacrificial silicon oxide layer was etched with a SCF-based etching composition of the present invention, illustrating a free standing microstructure.

[0014] Figure 3 is a control sample before SCF-based etching composition processing including a silicon substrate, a 100 nm thick silicon oxide film on the substrate and a 100 nm thick polysilicon film on the oxide.

[0015] Figure 4 is the control sample in Figure 3 after the sacrificial silicon oxide layer was etched with a SCF-based etching composition of the present invention, illustrating a free standing microstructure.

[0016] Figure 5 is a sample etched with a SCF-based etching composition of the present invention, illustrating a free standing microstructure.

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

[0017] The present invention is based on the discovery of supercritical fluid (SCF)-based etching compositions that are highly efficacious for the etching of sacrificial silicon-containing layers from semiconductor substrates. The compositions and methods of the invention are effective for etching sacrificial layers, including silicon and silicon oxide layers, and related post-etch residue removal from patterned wafers.

[0018] Because of its readily manufactured character and its lack of toxicity and negligible environmental effects, supercritical carbon dioxide (SCCO₂) is a preferred SCF in the broad practice of the present invention, although the invention may be practiced with any suitable SCF species, with the choice of a particular SCF depending on the specific application involved. Other preferred SCF species useful in the practice of the invention include oxygen, argon, krypton, xenon, and ammonia. Specific reference to SCCO₂ hereinafter in the broad description of the invention is meant to provide an illustrative example of the present invention and is not meant to limit the same in any way.

[0019] SCCO₂ might at first glance be regarded as an attractive reagent for removal of oxides and residue contaminants, since SCCO₂ has the characteristics of both a liquid and a gas. Like a gas, it diffuses rapidly, has low viscosity, near-zero surface tension, and penetrates easily into deep trenches and vias. Like a liquid, it has bulk flow capability as a “wash” medium.

[0020] However, despite these ostensible advantages, SCCO₂ is non-polar. Accordingly, it will not solubilize many polar species, including ionic etchant species comprising fluoride or inorganic salts and polar organic compounds that are present in many post-etch and post-ash residues. The non-polar character of SCCO₂ thus poses an impediment to its use for etching sacrificial layers and the subsequent cleaning of wafer surfaces of contaminant residues.

[0021] The present invention, however, is based on the discovery that disadvantages associated with the non-polarity of SCCO₂ and other SCFs can be overcome by appropriate formulation of SCF-based etching compositions with additives as hereinafter more fully

described, and the accompanying discovery that etching a sacrificial silicon-containing layer with a SCF-based medium is highly effective and achieves damage-free, residue-free etching of the substrate having such sacrificial silicon-containing layer thereon.

[0022] In one aspect, the invention relates to SCF-based etching compositions useful in removing sacrificial silicon-containing layers from a semiconductor substrate. The formulation of the present invention comprises a SCF, at least one co-solvent, at least one etchant, and optionally at least one surfactant, present in the following ranges, based on the total weight of the composition:

component of	% by weight
SCF	about 75.0% to about 99.5%
co-solvent	about 0.3% to about 22.5%
etchant	about 0.01% to about 5.0%
surfactant	about 0.01% to about 5.0%

[0023] In the broad practice of the invention, the SCF-based etching formulations may comprise, consist of, or consist essentially of a SCF, at least one co-solvent, at least one etchant and optionally at least one surfactant.

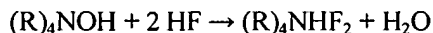
[0024] The inclusion of the co-solvent with the SCF serves to increase the solubility of the composition for sacrificial silicon-containing species. In general, the specific proportions and amounts of SCF, co-solvent, etchant, and optionally surfactant, in relation to each other may be suitably varied to provide the desired etching action of the SCF-based etching composition for the silicon oxide species and/or processing equipment, as readily determinable within the skill of the art without undue effort.

[0025] The co-solvent used in the SCF-based etching composition is preferably an alcohol. In one embodiment of the invention, such alcohol includes a straight-chain or branched C₁-C₆ alcohol (i.e., methanol, ethanol, isopropanol, etc.), or a mixture of two or more of such alcohol species. In a preferred embodiment, the alcohol is methanol or isopropanol (IPA).

[0026] With regards to conventional silicon oxide etching solutions, the etchant of choice is HF, which dissociates in water to form the etchant species F⁻, H₂F⁻ and H₂F₂. However, in a CO₂ rich environment, the ionization of HF to form etchant species does not readily occur

because the water reacts with the CO₂ (to form carbonic acid (H₂CO₃)) or is removed by the alcohol co-solvent.

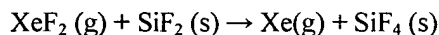
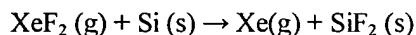
[0027] As such, the silicon oxide etchant used in the SCF-based etching composition of the present invention includes a pre-ionized fluoride source, such as a bifluoride species, including ammonium difluoride and tetraalkylammonium difluorides, such as those produced by the following reaction:



where R is methyl, ethyl, butyl, phenyl or fluorinated C₁-C₄ alkyl groups.

[0028] With regards to conventional silicon etching solutions, XeF₂ is particularly well suited to MEMS applications. XeF₂ etchants exhibit nearly infinite selectivity of silicon to photoresist, silicon oxides, silicon nitrides and aluminum. Being a vapor phase etchant, XeF₂ avoids many of the problems typically associated with wet processes. For example, XeF₂ surface tension forces are negligible and thus stiction between the microstructure and the substrate is less likely. In addition, etching rates using XeF₂ are much faster.

[0029] It has been proposed that XeF₂ etching of silicon involves the physisorption of XeF₂ onto the silicon surface. Because the bond energies of both the F atoms to the Xe atoms and the Si atoms to other Si atoms are sufficiently weak, and the attraction forces between Si and F are relatively strong, F will dissociate from Xe and bond to Si to form various silicon fluoride products, as illustrated in the following reactions:



An etching reaction occurs when volatile SiF₄ is formed, which leaves the surface spontaneously, thus removing sacrificial silicon material.

[0030] Notably, the XeF₂ etch rate is highly dependent on the dryness of the silicon surface. If water is present on the surface of the silicon, a thin silicon fluoride polymer layer forms. Accordingly, the broad practice of the invention includes wafer surface drying prior to exposure to XeF₂. SCCO₂ provides an efficient and environmentally safe way to dehydrate the wafer surface, thus eliminating the formation of the unwanted silicon fluoride polymer layer.

Further, pre-drying the silicon surface with SCCO_2 is also a necessary safety measure since most XeF_2 contains small amounts of XeF_4 , which upon reaction with water forms the contact explosive XeO_3 .

[0031] Species such as XeF_2 are largely insoluble in the non-polar SCF solvents. Accordingly, co-solvents are added to the composition to increase the solubility of XeF_2 in the silicon SCF-based etching composition of the present invention.

[0032] Surfactants are optionally added when the sacrificial silicon-containing layer includes silicon oxide. The surfactant used in the SCF-based etching composition may include nonionic surfactants, such as fluoroalkyl surfactants, polyethylene glycols, polypropylene glycols, polyethylene or polypropylene glycol ethers, carboxylic acid salts, dodecylbenzenesulfonic acid or salts thereof, polyacrylate polymers, dinonylphenyl polyoxyethylene, silicone or modified silicone polymers, acetylenic diols or modified acetylenic diols, and alkylammonium or modified alkylammonium salts, as well as combinations comprising at least one of the foregoing surfactants. In a preferred embodiment, the surfactant is a modified acetylenic diol.

[0033] In one embodiment, the silicon dioxide etching composition of the invention includes SCCO_2 , methanol, ammonium bifluoride, and a modified acetylenic diol.

[0034] In another embodiment, the silicon etching composition of the invention includes SCCO_2 , methanol and XeF_2 .

[0035] In another aspect, the invention relates to methods of removal of sacrificial silicon-containing layers including, but not limited to, silicon, silicon oxide and post-ash and post-etch residues, from a semiconductor substrate using the appropriate SCF-based etching composition.

[0036] The sacrificial silicon-containing layers and/or post-ash and post-etch residues may be removed using a SCF-based etching composition including a SCF, at least one co-solvent, at least one etchant, and optionally at least one surfactant, as described herein. Another possible application is removal of SiO_2 particles via reaction or dissolution.

[0037] At present, the favored technique to remove developed photoresist is plasma ashing. Plasma ashing involves exposing the photoresist-covered wafer to oxygen plasma in

order to oxidatively decompose the unexposed photoresist film from the substrate surface. However, plasma etching usually results in the formation of plasma-ash and plasma-etch residue, and this residue must subsequently be removed.

[0038] The removal of post-ash and post-etch residue is a well known problem in light of the continuing and rapid decrease in critical dimensions of microelectronic device structures, since any residue remaining on the substrate can render the final device deficient or even useless for its intended purpose.

[0039] Conventional post-ash and post-etch residue cleaning by wet chemical treatment has not proven wholly satisfactory in effecting complete removal of residues from the substrate, especially from trenches, vias and microstructures in low k dielectrics. Further, these conventional cleaning approaches are time-consuming, costly, require substantial amounts of chemical reagents for the cleaning operation and produce substantial quantities of chemical waste.

[0040] The SCF-based compositions of the present invention overcome the disadvantages of the prior art post-ash and post-etch residue removal treatments for Si and SiO₂ based residues.

[0041] The appropriate SCF-based etching composition can be employed to contact a substrate having a sacrificial layer, e.g., silicon oxide or silicon, and/or post-ash and post-etch residue, at a pressure in a range of from about 1400 to about 4400 psi for sufficient time to effect the desired etching of the sacrificial layer and/or residue, e.g., for a contacting time in a range of from about 30 seconds to about 30 minutes and a temperature of from about 40 to about 70°C, although greater or lesser contacting durations and temperatures may be advantageously employed in the broad practice of the present invention, where warranted.

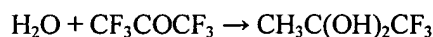
[0042] The removal process in a particularly preferred embodiment includes sequential processing steps including dynamic flow of the SCF-based etching composition over the substrate having the sacrificial layer and/or residue, followed by a static soak of the substrate in the SCF-based etching composition, with the respective dynamic flow and static soak steps being carried out alternatingly and repetitively, in a cycle of such alternating steps.

[0043] A “dynamic” contacting mode involves continuous flow of the cleaning composition over the wafer surface, to maximize the mass transfer gradient and effect complete removal of the sacrificial layer and/or residue from the substrate. A “static soak” contacting mode involves contacting the wafer surface with a static volume of the etching composition, and maintaining contact therewith for a continued (soaking) period of time.

[0044] For example, the dynamic flow/static soak steps may be carried out for four successive cycles in the aforementioned illustrative embodiment, as including a sequence of 30 sec-10 min dynamic flow, 30 sec-5 min high pressure static soak, e.g., about 3000 psi to about 4400 psi, 30 sec-10 min dynamic flow, and 30 sec-10 min low pressure static soak, e.g., about 1400 psi to about 2800 psi.

[0045] With regards to the silicon layers to be etched, the wafer surface should be dehydrated prior to the etching process. SCFs can be used as drying media for patterned wafers in drying compositions that include one or more water-reactive agents that chemically react with water on the patterned wafer to form reaction product species that are more soluble in the SCF than water.

[0046] As an illustrative example, hexafluoroacetone (HFA) is usefully employed as a water-reactive agent in SCCO_2 to provide a highly effective SCF composition for drying of patterned wafers. In such composition, HFA reacts instantly with water and quantitatively forms a soluble and volatile diol as depicted in the following reaction:



[0047] The product diol, $\text{CH}_3\text{C}(\text{OH})_2\text{CF}_3$, is highly soluble in SCCO_2 and is readily dissolved by the SCF, thereby effectively removing water from the patterned wafer substrate with which the SCF composition, containing SCCO_2 and HFA, is contacted.

[0048] More generally, the water-reactive agent in the SCF-based wafer drying composition can be of any suitable type, including for example, other halogenated aldehydes and ketones; halogenated diketones, e.g., 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, alternatively denoted as (hfac)H; halogenated esters; carboxylic anhydrides, e.g., $(\text{CH}_3\text{CO})_2\text{O}$; siloxanes,

halogenated silanes; and any other compounds and materials that easily react with water and form derivatives soluble in SCCO_2 or other SCF species.

[0049] Generally, the water-reactive agent can be formulated in the SCF-based wafer drying composition at any suitable concentration that is effective for water removal from the patterned wafer substrate. In various embodiments, depending on the particular SCF species employed, the concentration of the water-reactive agent can be a concentration in a range of from about 0.01 to about 10.0 % by weight, based on the total weight of the supercritical fluid and the water-reactive agent, with concentrations of from about 0.1 to about 7.5 % by weight, on the same total weight basis being more preferred, and from about 0.1 to about 5.0 % by weight, on the same total weight basis being most preferred.

[0050] The contacting of the patterned substrate with the drying composition is carried out for a suitable period of time, which in a specific embodiment can for example be on the order of from about 20 to about 60 seconds, although other (longer or shorter) periods of contacting may be usefully employed depending on the nature and amount of the water to be removed from the patterned substrate, and the process conditions employed for drying.

[0051] Following drying of the patterned substrate, the contacting vessel in which the SCF-based wafer drying composition is contacted with the patterned substrate can be rapidly decompressed to separate the SCF composition from the patterned substrate and exhaust the regasified SCF from the contacting vessel, so that the non-supercritical component(s), such as the soluble water reaction product(s), can be entrained in the regasified SCF and likewise be removed from the drying locus. Thereafter, the contacting vessel can be compressed and the SCF-based etching composition may be introduced to the vessel to remove the sacrificial layer and/or residue.

[0052] Following the contacting of the etching composition with the substrate bearing the sacrificial layer and/or residue, the substrate thereafter preferably is washed with copious amounts of SCF/methanol/deionized water solution in a first washing step, to remove any residual precipitated chemical additives from the substrate region in which etching and/or residue removal has been effected, and finally with copious amounts of pure SCF, in a second

washing step, to remove any residual methanol co-solvent and/or precipitated chemical additives from the substrate region. Preferably, the SCF used for washing is SCCO_2 .

[0053] The SCF-based etching compositions of the present invention are readily formulated by simple mixing of ingredients, e.g., in a mixing vessel under gentle agitation.

[0054] Once formulated, such etching compositions are applied to the substrate for contacting with the sacrificial layer and/or residue thereon, at suitable elevated pressures, e.g., in a pressurized contacting chamber to which the etching composition is supplied at suitable volumetric rate and amount to effect the desired contacting operation for removal of the sacrificial layer and/or residue.

[0055] It will be appreciated that specific contacting conditions for the etching compositions of the invention are readily determinable within the skill of the art, based on the disclosure herein, and that the specific proportions of ingredients and concentrations of ingredients in the etching compositions of the invention may be widely varied while achieving desired removal of the sacrificial layer and/or residue from the substrate.

[0056] The features and advantages of the invention are more fully shown by the illustrative example discussed below.

[0057] The sample wafers examined in this study included a substrate, a 100 nm thick silicon oxide film on the substrate and a 100 nm polysilicon film on top of the oxide layer. The samples were processed to etch the sacrificial silicon oxide layer using the SCF-based etching composition of the following formulation:

Component	Weight Percent
ammonium bifluoride (32.3 wt %)	1.0 %
surfynol-104	0.05 %
methanol	4.0 %
SCCO_2	94.95%

[0058] Alternatively, the sample wafers may include a substrate, a 380 nm thick silicon film on the substrate, a 30 nm silicon oxide film on the silicon film, and a 300 nm silicon nitride film on top of the oxide layer. The samples may be processed to etch the sacrificial silicon oxide layer using the SCF-based etching composition of the following formulation:

Component	Weight Percent
ammonium bifluoride (32.3 wt %)	1.0 %
surfynol-104	0.05 %
methanol	4.0 %
SCCO ₂	94.95%

[0059] The temperature was maintained at 50°C throughout the cleaning/rinsing procedure. The optimal process conditions are dynamic flow of the SCF-based etching composition for 45 sec at 4000 psi followed by a 1 min SCCO₂ rinse. The samples were then thoroughly rinsed with copious amounts of SCCO₂/methanol/deionized water and pure SCCO₂ in order to remove any residual co-solvent and/or precipitated chemical additives.

[0060] The results are shown in Figures 1-5, as described hereinbelow.

[0061] Figures 1 and 3 are optical microscope photographs of control wafers prior to etching, showing unremoved sacrificial silicon oxide layers.

[0062] Figures 2 and 4 show the optical image of the Figures 1 and 3 wafers after sacrificial silicon oxide layer removal, respectively, using the composition and method described herein. Following removal of the sacrificial silicon oxide layer, the free standing, stiction-free microstructures can be clearly seen.

[0063] Figure 5 is an optical image of a free-standing microstructure produced using the composition and method of the present invention.

[0064] The above-described photographs thus evidence the efficacy of SCF-based etching compositions in accordance with the invention, for removal of sacrificial layers from wafer substrates.

[0065] Accordingly, while the invention has been described herein in reference to specific aspects, features and illustrative embodiments of the invention, it will be appreciated that the utility of the invention is not thus limited, but rather extends to and encompasses numerous other aspects, features and embodiments. Accordingly, the claims hereafter set forth are intended to be correspondingly broadly construed, as including all such aspects, features and embodiments, within their spirit and scope.